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METHOD FOR MANUFACTURING HIGHLY ELECTROCONDUCTIVE ANILINE
GROUP POLYMER
[Kododensei Anirinkei Porima No Seizoho]

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Specification

1. Title of the invention

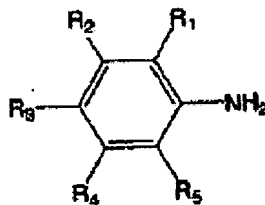
Method for Manufacturing Highly Electroconductive
Aniline Group Polymer

2. Claims

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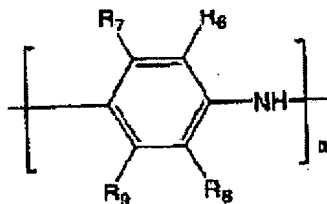
1. A method for manufacturing a highly electroconductive aniline group polymer, characterized by the fact that in a method that polymerizes at least one kind of compound (i) selected from a group comprised of acidic group-substituted aniline, its alkali metal salt, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt represented by a general formula (1)

(Structure 1)



(in the formula, R1, R2, R3, R4, and R5 are selected from a group comprised of hydrogen, straight-chain or branched alkyl group having 1-24 carbons, straight-chain or branched alkoxy group having 1-24 carbons, acidic group, hydroxyl group, nitro group, and halogen; at least one of them represents an acidic group; and here, the acidic group represents a sulfonic acid group or carboxyl group) with an oxidizer in a solution containing a basic compound (ii) and a solvent (iii) and manufactures an aniline group polymer with an average degree of polymerization of $n = 10$ or more and a weight average molecular weight of 5,000 or more represented by a general formula (2)

(Structure 2)



(in the formula, R6, R7, R8, and R9 are selected from a group comprised of hydrogen, straight-chain or branched alkyl group having 1-24 carbons, straight-chain or branched alkoxy group having 1-24 carbons, acidic group, hydroxyl

group, nitro group, and halogen; at least one of them represents an acidic group; and here, the acidic group represents a sulfonic acid group or carboxyl group), the polymerization is carried out in a system in which the oxidizer exists at a mole ratio of an equal mole or more to the above-mentioned (i).

2. The method for manufacturing a highly electroconductive aniline group polymer of Claim 1, characterized by the fact that pH of the polymerization system is maintained at 7 or less.

3. The method for manufacturing a highly electroconductive aniline group polymer of Claim 1 or 2, characterized by the fact that a mixed solution of at least one kind of compound (i) selected from a group comprised of acidic group-substituted aniline, its alkali metal salt, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt, the basic compound (ii), and the solvent (iii) is added into an oxidizer solution.

4. The method for manufacturing a highly electroconductive aniline group polymer of any of Claims 1-3, characterized by the fact that the polymerization is carried out in the

coexistence of proton acid (iv) in the polymerization system.

5. The method for manufacturing a highly electroconductive aniline group polymer of any of Claims 1-4, characterized by the fact that the reaction temperature during the polymerization is maintained at 50°C or lower.

3. Detailed explanation of the invention

[0001]

(Technical field of the invention)

The present invention pertains to a method for manufacturing a solvent-soluble electroconductive aniline group polymer. A solution mainly composed of the polymer being obtained by the method of the present invention is spread on a base material by a simple method such as spray coating method, dip coating method, roll coating method, gravure coating method, reverse coating method, roll brush method, air knife coating method, and curtain coating method, so that an electric conductor can be formed. Also, in order to improve the adhesion and the coated film strength of the electroconductive film, an appropriate binder polymer can also be mixed and used when spreading.

[0002] As the base material for spreading, various kinds of plastics, for example, polyester resin such as PET and PEN, polyolefin resin represented by polyethylene and polypropylene, polyvinyl chloride, nylon, polystyrene, polycarbonate, epoxy resin, fluororesin, polysulfone, polyimide, polyurethane, phenol resin, amino resin, silicon resin, and synthetic papers, films, papers, iron, aluminum, copper, nickel, stainless steel, etc., are mentioned. The spreading process may be carried out before or during the manufacturing processes of these base materials, for example, uniaxial stretching method, biaxial stretching method, molding process, embossing process, etc., and may also be applied to the base material on which these treatment processes have been completed.

[0003] Also, the composition mainly composed of the polymer being obtained by the method of the present invention can be applied to the field of various kinds of antistatic and anti-electrostatic usages, condensers, batteries, EMI shields, chemical sensors, nonlinear materials, display devices, anticorrosives, adhesives, fibers, antistatic paints, electrodeposited paints, plated primers, undercoats of electrostatic paints, electric corrosion resistance, storage performance improvement of batteries, etc. Furthermore, since the polymer being obtained by the method

of the present invention has no temperature tendency of the electric conductivity, has high transparency, and can be stretched, molded, embossed, etc., the suitability for various kinds of antistatic usages is excellent.

[0004] As examples for antistatic agents using the polymer being used by the method of the present invention, packing materials, magnetic cards, magnetic tapes, magnetic disks, photographic films, printing materials, mold release films, heat seal tapes, IC trays, IC carrier tapes, cover tapes, etc., are mentioned.

[0005]

(Prior art)

As the electroconductive polymer, a doped polyaniline is well known, however it is insoluble in almost all the solvents and has a difficulty in molding and working. Also, in methods for applying an electrolytic oxidation polymerization to aniline (Japanese Kokai Patent Application No. Sho 60[1085]-235831, J. PolymerSci. Polymer Chem. Ed., 26, 1531 (1988)), though the polyaniline polymer can be formed on an electrode, its isolation operation is complicated, and its large amount of synthesis is difficult.

[0006] Also, sulfonated polyaniline and its synthesizing method and carboxylated polyaniline and its synthesizing

method, which are self-doping, soluble in an alkali, and exerts an electric conductivity without adding a doping agent, have recently been proposed.

[0007] For example, as methods for synthesizing the sulfonated polyaniline, a method that synthesizes a sulfonated polyaniline by electrochemically polymerizing aniline and m-aminobenzenesulfonic acid (Journal of Japan Chemical Society, 1985, 1124, Japanese Kokai Patent Application No. Hei 02[1990]-166165), a method that synthesizes a sulfonated polyaniline by respectively, independently, electrochemically polymerizing o-, m-, or p-aminobenzenesulfonic acid (Japan Chemical Society, the 64th Fall Annual Lecture Preprint Collection II 706 (1992)), a method that synthesizes a sulfonated polyaniline by chemically polymerizing aniline and o- or m-aminobenzenesulfonic acid (Japanese Kokai Patent Application No. Hei 1[1999]-301714), a method that applies a chemical oxidation polymerization to an aminobenzenesulfonic acid group compound or a monomer containing an aminobenzenesulfonic acid group compound and an aniline group compound (Japanese Kokai Patent Application No. Hei 6 [1994]-56987), a method that sulfonates an emerald type polymer (polyaniline) with a rich sulfuric acid (Japanese Kokai Patent Application No.

Sho 58[1983]-210902), a method that sulfonates a sulfuric anhydride/triethyl phosphate complex (Japanese Kokai Patent Application No. Sho 61[1987]-197633), a method that carries out a sulfonation with fuming sulfuric acid (J. Am. Chem. Soc., (1991) 113, 2665-2671, J. Am. Chem. Soc., (1990)112, 2800, WO91-06887), a method that chemically polymerizes diphenylamine-4-sulfonic acid (sodium salt) and synthesizes a N-substitutional (Polymer, (1993) 34, 158-162), etc., are known.

[0008] In the method that synthesizes a sulfonated polyaniline by electrochemically polymerizing aniline and m-aminobenzenesulfonic acid (Journal of Japan Chemical Society, 1985, 1124, Japanese Kokai Patent Application No. Hei 02[1990]-166165), since the product is formed on an electrode, its isolation operation is complicated, and its large amount of synthesis is difficult.

[0009] Also, in Japan Chemical Society, the 64th Fall Annual Lecture Preprint Collection II 706 (1992), the method that synthesizes a soluble electroconductive polymer by an electrolytic oxidation of aminobenzenesulfonic acid is explained, however it is also difficult to say that this method is suitable for the synthesis at a large amount. Also, it is described that when the aminobenzenesulfonic acid was subjected to a chemical oxidation polymerization

by using ammonium benzoxydisulfate as an oxidizer, no product could be obtained. Also, according to J. Am. Chem. Soc., (1991) 113, 2665-2671, it is described that an attempt of chemically and electrochemically polymerizing o- or m-aminobenzenesulfonic acid was made, however it was not successful.

[0010] Also, in Japanese Kokai Patent Application No. Hei 6 [1994]-56987, it is described that a water-soluble electroconductive polymer can be obtained by applying a chemical oxidation polymerization to an aminobenzenesulfonic acid group compound or a monomer containing an aminobenzenesulfonic acid group compound and an aniline group compound in any of acidic, neutral, and alkali solutions. However, according to the review of these inventors, the polymerization in the presence of a basic compound is essential to obtain a polymer with a sufficient molecular weight for forming a film, and a polymer with a sufficient molecular weight could be obtained for forming a film in an acidic solution and a neutral solution.

[0011] In application examples of Japanese Kokai Patent Application No. Hei 6 [1994]-56987, the polymerization in a sulfuric acid solution is carried out in all of the application examples, and there is no application example

for the polymerization in an alkali solution. Also, even in the application examples for the polymerization in an acidic aqueous solution, since there is no description about the molecular weight, the properties of the polymers obtained are not clarified.

[0012] Furthermore, these inventors attempted the polymerization in an aqueous solution containing a proton acid and in an aqueous solution by using ammonium peroxodisulfate as an oxidizer, and as result, though a polymer soluble in water was obtained, a practical polymer for forming a film could not be obtained due to its low molecular weight.

[0013] As a result of an additional test of the method that synthesizes a sulfonated polyaniline by chemically polymerizing aniline and m-aminobenzenesulfonic acid with ammonium peroxodisulfate described in Japanese Kokai Patent Application No. Hei 1[1999]-301714 and the method that chemically polymerizes aniline and m-aminobenzenesulfonic acid with potassium permanganate described in Japanese Kokai Patent Application No. Hei 6 [1994]-56987 by these inventors, only about one sulfonic acid group was introduced into five aromatic rings, and though the electric conductivity was exhibited, they were completely insoluble in neutral and acidic waters and were little

soluble in an alkaline aqueous solution such as ammonia water.

[0014] Also, the sulfonation by the method of Japanese Kokai Patent Application No. Sho 61[1987]-197633 is described in page 7 of said publication, and since the solubility of polyaniline to a reaction solvent and the reaction is carried out in a dispersed state, only about one sulfonic acid group is introduced into five aromatic rings. The sulfonated polyaniline with a small introduction ratio of the sulfonic acid group being obtained in this manner does not have sufficient electric conductivity and solubility.

[0015] Also, according to J. Am. Chem. Soc., (1991) 113, 2665-2671 and

J. Am. Chem. Soc., (1990)112, 2800, it is described that when polyaniline is sulfonated with fuming sulfuric acid, about one sulfonic acid group is introduced into two aromatic rings. However, to sufficiently sulfonate the polyaniline by this method, since the solubility of the polyaniline in the fuming sulfuric acid is not sufficient, a very excessive amount of fuming sulfuric acid is required. Also, when the polyaniline is added to the fuming sulfuric acid, the polymer is easily solidified. /4 Furthermore, the polymerized product and its sulfonated

product synthesized in this method are dissolved in an aqueous solution containing a base such as ammonia and alkylamine, however they are not dissolved in water alone. [0016] Also, according to Polymer (1993)34, 158-162, in case diphenylamine-4-sulfonic acid (sodium salt) is polymerized, a N-position substituted sulfonated polyaniline with a structure in which one benzenesulfonic acid is substituted for an aniline skeleton is obtained. It is described that though the polymerized product is dissolved in water alone, a super centrifugal separation operation is required for the isolation of the polymerized product. As a result of an addition test by these inventors, owing to its high solubility, the acquisition yield of the polymerized product from the polymerization solvent was low, and the polymerized product could not be isolated without the high-speed centrifugal separation operation. Also, due to the N-position substitution type, the electric conductivity was low, compared with the polymerized product synthesized by the method of the above-mentioned Am. Chem. Soc., (1991) 113, 2665-2671.

[0017] Also, for example, as a method for synthesizing carboxylated polyaniline, a manufacturing method that oxidation-polymerizes 2- or 3-carboxyaniline or its salt, treats it with a basic substance, and obtains a carboxyl

group by a salt (Japanese Kokai Patent Application No. Hei 4[1992]-268331) is proposed. However, as the amount of oxidizer being used, twice equivalent or more is required for the raw material, and the electric conductivity value is low. Thus, it is considered that the reactivity of the monomer is low and the polymer with a low molecular weight is generated.

[0018] Also, a synthesizing method that polymerizes methyl anthranilate (methyl ester anthranilate) in an acidic aqueous solvent in the presence of ammonium peroxodisulfate and gels methyl ester by an alcoholic potassium hydroxide (Japanese Kokai Patent Application No. Hei 5[1993]-226238) is proposed, however since the reaction has two stages, the operation is very complicated.

[0019] Furthermore, according to these inventors, as a result of an attempt of polymerizing ammonium peroxodisulfate in an aqueous solution containing proton acid by using 2-carboxyaniline as an oxidizer, no product could be obtained. Also, as a result of an attempt of aniline and 2-carboxyaniline in an aqueous solution containing proton acid by using 2-carboxyaniline as an oxidizer, a copolymer could be obtained, however both its solubility and electric conductivity were low. Therefore, it is considered that in order to exert the electric

conductivity without adding a doping agent to the polymer and to improve the solubility, it is necessary to introduce much more acidic groups such as sulfonic acid group or carboxyl group into aromatic rings of the main chain.

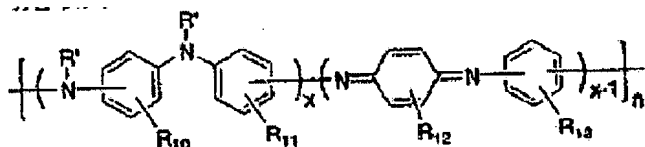
[0020] Also, in case the moldability of films being molded by spreading is considered, the solubility in both water and organic solvents is desirable for being able to be spread especially on any of hydrophilic and hydrophobic base materials. On the other hand, though the sulfonated product of polyaniline has a solubility in alkali water, it is insoluble in neutral and acidic aqueous solutions, and it cannot be said that the solubility in an organic solvent is sufficient.

[0021] As a method to solve these problems, these inventors proposed a method for manufacturing an aniline group copolymer sulfonated product characterized by copolymerizing at least one kind of compound selected from a group comprised of aniline, N-alkylaniline, and phenylenediamines and aminobenzenesulfonic acid in an acidic solvent by using an oxidizer and sulfonating it with a sulfonating agent (Japanese Kokai Patent Application No. Hei 5[1993]-178989). However, in this method, a sulfonation operation in a rich sulfuric acid is required,

and the treatment of a waste acid remains as a large problem.

[0022] Also, any of the copolymers synthesized by the above-mentioned method is presumed to have a structure of the following formula (3).

(Structure 3)



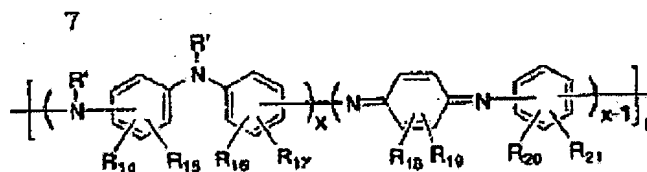
(In the formula, R10, R11, R12, and R13 are respectively selected from a group comprised of hydrogen and a sulfonic acid group, R' is selected from a group comprised of hydrogen or an alkyl group having 1-24 carbons, the ratio of the sulfonic acid group has a content of 40-80% to aromatic rings, x represents an arbitrary number of 0-1, and n represents a number of 2-1500 showing the degree of polymerization.)

[0023] Furthermore, these inventors proposed a method for manufacturing an aniline group copolymer characterized by the fact that a sulfonation operation for generating a large amount of waste matter is omitted by copolymerizing

at least one kind of compound selected from a group comprised of aniline, N-alkylaniline, and phenylenediamines and an alkoxy group-substituted aminobenzenesulfonic acid (Japanese Kokai Patent Application No. Hei 6[1994]-293828). However, the copolymer being obtained by this method is not dissolved in water alone.

[0024] Also, any of the copolymers synthesized by the above-mentioned method is presumed to have a structure of the following formula (4).

(Structure 4)



/5

(In the formula, R14, R16, R17, R18, R19, R20, and R21 are respectively selected from a group comprised of hydrogen, alkoxy group, and sulfonic acid group, the ratio of the sulfonic acid group has a content of 25-50% to aromatic rings and includes an alkoxy group and a sulfonic acid group in the same aromatic ring, R' is selected from a

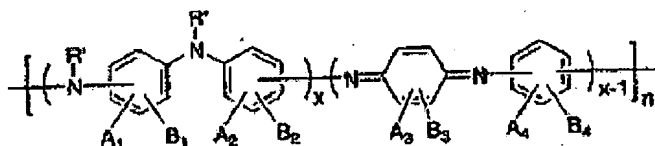
group comprised of hydrogen or an alkyl group having 1-4 carbons, x represents an arbitrary number of 0-1, and n represents a number of 2-1500 showing the degree of polymerization.)

[0025] Also, these inventors proposed a soluble aniline group electroconductive polymer and its manufacturing method characterized by the fact that an acidic group-substituted aniline such as sulfonic acid group-substituted aniline or carboxyl group-substituted aniline is polymerized in a solution containing a basic compound (Japanese Kokai Patent Application Nos. Hei 7[1995]-196791 and Hei 7[1995]-324132) were proposed. This method is contradictory to an established theory in which anilines having a sulfonic acid group or carboxyl group are difficult to be polymerized alone and can manufacture a polymer with a high-molecular weight. Furthermore, the soluble electroconductive polymer obtained exhibits excellent dissolution in any of acidic and alkali aqueous solutions. However, in this method, the generation of a side reaction and the by-production of an oligomer component being considered based on the side reaction are not completely suppressed, so that impurities are mixed into the polymer and the electric conductivity improvement

is hindered. Also, the process for removing these impurities is complicated.

[0026] Also, any of the copolymers synthesized by the above-mentioned method is presumed to have a structure.

(Structure 5)



(In the formula, A1-A4 represent one group selected from sulfonic acid, carboxyl group, these alkali metal salts, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt, B1-B4 represent one group selected from a group comprised of hydrogen, straight-chain or branched alkyl group having 1-4 carbons, straight-chain or branched alkoxy group having 1-4 carbons, acidic group, hydroxyl group, nitro group, and halogen group, x represents an arbitrary number of 0-1, and n represents a number of 2-5000 showing the degree of polymerization.)

[0027]

(Problems to be solved by the invention)

The purpose of the present invention is to provide a simple method for manufacturing an aniline group polymer that exhibits excellent solubility in water or organic solvents with any pH, has high electric conductivity, has a high molecular weight and a narrow molecular weight distribution, has a high purity, and is excellent in film formability.

[0028]

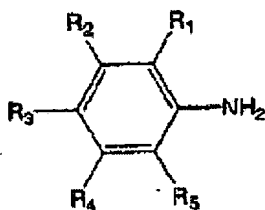
(Means to solve the problems)

These inventors reviewed simple methods for manufacturing an acidic group-substituted polyaniline with a large introduction ratio of an acidic group such as sulfonic acid group and/or carboxyl group to an aromatic ring as polyaniline having high electric conductivity and solubility in earnest. As a result, it was elucidated that since the reaction method that dropped an oxidizer into a monomer solution containing a basic compound in the conventional method, pH in the system at the initial stage of the polymerization was basic, a side reaction such as azotization was easily caused by an acidic group-substituted aniline as a raw material monomer for that reason, and an oligomer component was generated by the

azotization reaction. Furthermore, it was discovered that with an oxidation polymerization in a system in which an oxidizer existed at an equal mole or more to an acidic group-substituted aniline such as sulfonic acid group-substituted aniline and/or carboxyl group-substituted containing a basic compound, the above-mentioned side reaction was suppressed and a polymer with high purity and a molecular weight distribution close to a monodisperse. Also, it was discovered that since a side reaction was difficult to be generated in this reaction, impurities and oligomer component were difficult to be generated, so that a polymer in which the average molecular weight was improved, the electric conductivity was largely improved, and the hue and the film formability were also improved could be manufactured. Then, the present invention was completed.

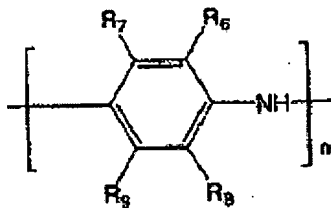
[0029] In other words, the present invention pertains to a method for manufacturing a highly electroconductive aniline group polymer characterized by the fact that in a method that polymerizes at least one kind of compound (i) selected from a group comprised of acidic group-substituted aniline, its alkali metal salt, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt represented by a general formula (1)

(Structure 6)



(in the formula, R1, R2, R3, R4, and R5 are selected from a group comprised of hydrogen, straight-chain or branched alkyl group having 1-24 carbons, straight-chain or branched alkoxy group having 1-24 carbons, acidic group, hydroxyl group, nitro group, and halogen; at least one of them represents an acidic group; and here, the acidic group represents a sulfonic acid group or carboxyl group) /6 with an oxidizer in a solution containing a basic compound (ii) and a solvent (iii) and manufactures an aniline group polymer with an average degree of polymerization of $n = 10$ or more and a weight average molecular weight of 5,000 or more represented by a general formula (2)

(Structure 7)



(in the formula, R₆, R₇, R₈, and R₉ are selected from a group comprised of hydrogen, straight-chain or branched alkyl group having 1-24 carbons, straight-chain or branched alkoxy group having 1-24 carbons, acidic group, hydroxyl group, nitro group, and halogen; at least one of them represents an acidic group; and here, the acidic group represents a sulfonic acid group or carboxyl group), the polymerization is carried out in a system in which the oxidizer exists at a mole ratio of an equal mole or more to the above-mentioned (i).

[0030]

(Embodiment of the invention)

Next, the manufacturing method of the present invention is explained in further detail. The most representative example as

at least one kind of compound (i) selected from a group comprised of acidic group-substituted aniline, its alkali metal salt, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt being used in the present invention is a sulfonic acid-substituted aniline or carboxyl group-substituted aniline. An aminobenzenesulfonic acid derivative exhibits a high electric conductivity tendency, compared with an aminobenzoic acid derivative, whereas the aminobenzonic acid derivative exhibits a high solubility tendency, compared with the aminobenzenesulfonic acid derivative. These derivatives can also be used by mixing at an optional ratio in accordance with the purposes.

[0031] As the sulfonic acid-substituted aniline, aminobenzenesulfonic acids such as o-, m-, or p-aminobenzenesulfonic acid, aniline-2,6-disulfonic acid, aniline-2,5-disulfonic acid, aniline-3,5-disulfonic acid, aniline-2,4-disulfonic acid, and aniline-3,4-disulfonic acid, alkyl-substituted aminobenzenesulfonic acids such as methylaminobenzenesulfonic acid, ethylaminobenzenesulfonic acid, n-propylaminobenzenesulfonic acid, isopropylaminobenzenesulfonic acid, n-butylaminobenzenesulfonic acid, sec-butylaminobenzenesulfonic acid, and t-

butylaminobenzenesulfonic acid, alkoxy group-substituted aminobenzenesulfonic acids such as methoxyaminobenzenesulfonic acid, ethoxyaminobenzenesulfonic acid, and propoxyaminobenzenesulfonic acid, hydroxy group-substituted aminobenzenesulfonic acids, nitro group-substituted aminobenzenesulfonic acids, halogen group-substituted aminobenzenesulfonic acids such as fluoroaminobenzenesulfonic acid, chloroaminobenzenesulfonic acid, and bromoaminobenzenesulfonic acid, etc., can be mentioned. Among them, aminobenzenesulfonic acids, alkyl group-substituted aminobenzenesulfonic acids, alkoxy group-substituted aminobenzenesulfonic acids, hydroxy group-substituted aminobenzenesulfonic acids, etc., are practically preferable. Also, these sulfonic acid group-substituted anilines may be respectively used alone or may also be used by mixing at an optional ratio of two kinds or more.

[0032] As the carboxyl group-substituted aniline, aminobenzenecarboxylic acids such as o-, m-, or p-aminobenzenecarboxylic acid, aniline-2,6-dicarboxylic acid, aniline-2,5-dicarboxylic acid, aniline-3,5-dicarboxylic acid, aniline-2,4-dicarboxylic acid, and aniline-3,4-dicarboxylic acid, alkyl-substituted aminobenzenecarboxylic

acids such as methylaminobenzenecarboxylic acid, ethylaminobenzenecarboxylic acid, n-propylaminobenzenecarboxylic acid, isopropylaminobenzenecarboxylic acid, n-butylaminobenzenecarboxylic acid, sec-butylaminobenzenecarboxylic acid, and t-butylaminobenzenecarboxylic acid, alkoxy group-substituted aminobenzenecarboxylic acids such as methoxyaminobenzenecarboxylic acid, ethoxyaminobenzenecarboxylic acid, and propoxyaminobenzenecarboxylic acid, hydroxy group-substituted aminobenzenecarboxylic acids, nitro group-substituted aminobenzenecarboxylic acids, halogen group-substituted aminoenzenecarboxylic acids such as fluoroaminobenzenecarboxylic acid, chloroaminobenzenecarboxylic acid, and bromoaminobenzenecarboxylic acid, etc., can be mentioned. Among them, aminobenzenecarboxylic acids, alkyl group-substituted aminobenzenecarboxylic acids, alkoxy group-substituted aminobenzenecarboxylic acids, hydroxy group-substituted aminobenzenecarboxylic acids, etc., are practically preferable. Also, these carboxylic acid group-substituted anilines may be respectively used alone or may

also be used by mixing at an optional ratio of two kinds or more.

[0033] More specifically, detailed examples of the positions and the combinations of substituents of the acidic group-substituted aniline of the above-mentioned general formula (1) are shown in Table 1.

11

R1	R2	R3	R4	R5
A A A A	B H H H	H B H H	H H B H	H H H B
H H H B	A A A A	B H H H	H B H H	H H H B
H H B H	H H H B	A A A A	B H H H	H B H H
H H H B	H H B H	H B H H	A A A A	B H H H
H H H B	H H B H	H B H H	B H H H	A A A A

(Table 1)

/7

Where, A: One group selected from sulfonic acid or carboxyl acid group, its alkali metal salt, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt;

B: One group selected from alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, and t-butyl group, alkoxy group such as methoxy group, ethoxy group, n-propoxy group, iso-propoxy group, n-butoxy group, sec-butoxy group, and t-butoxy group, and halogen group such as hydroxy group, fluoro group, chloro group, and bromo group; and

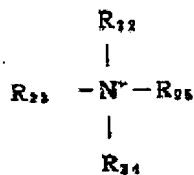
H: Hydrogen.

[0034] As alkali metals that can form salts by these monomers, lithium, sodium, and potassium can be mentioned, and as alkaline-earth metals, magnesium, calcium, etc., can be mentioned.

[0035] Also, as substituted ammoniums, fatty ammoniums, ring-shaped saturated ammoniums, ring-shaped unsaturated ammoniums, etc., are mentioned.

[0036] The above-mentioned fatty ammonium salts is represented by the following formula (6).

(Structure 8)



(In the formula, R22-R25 represent groups independently selected from a group comprised of hydrogen and alkyl groups having 1-4 carbons). For example, methyl ammonium, dimethyl ammonium, trimethyl ammonium, ethyl ammonium, diethyl ammonium, triethyl ammonium, methylethyl ammonium, diethylmethyl ammonium, dimethylethyl ammonium, propyl ammonium, dipropyl ammonium, isopropyl ammonium, diisopropyl ammonium, butyl ammonium, dibutyl ammonium, methylpropyl ammonium, ethylpropyl ammonium, methylisopropyl ammonium, ethylisopropyl ammonium, methylbutyl ammonium, ethylbutyl ammonium, tetramethyl ammonium, tetramethylol ammonium, tetraethyl ammonium, tetra n-butyl ammonium, tetra sec-butyl ammonium, tetra t-butyl ammonium, etc., can be mentioned. Among them, the case where one of R22-R25 is hydrogen and the other three

are alkyl groups having 1-4 carbons is most preferable, and the case where two of R22-R25 are hydrogens and the other two are alkyl groups having 1-4 carbons is preferable.

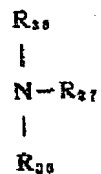
[0037] As the ring-shaped saturated ammoniums, piperidinium, pyrrolidinium, morpholium, piperazinium, and derivatives having these skeletons are mentioned.

[0038] As the ring-shaped unsaturated ammonium salts, pyridinium, α -picolinium, β -picolinium, γ -picolinium, quinolinium, isoquinolinium, pyrrolinium, and derivatives having these skeletons are mentioned.

[0039] Next, as the basic compound (ii) being used in the present invention, ammonia, fatty amines, ring-shaped saturated amines, ring-shaped saturated amines, inorganic base, etc., are used. In particular, fatty amines, ring-shaped saturated amines, ring-shaped unsaturated amines, etc., are preferable.

[0040] As preferable fatty amines, a compound represented by the following general formula (7)

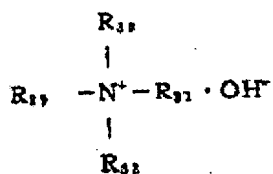
(Structure 9)



(in the formula, R26-R28 represent groups independently selected from a group comprised of alkyl groups having 1-4 carbons) or an ammonium hydroxide compound represented by a general formula (8)

/8

(Structure 10)



(in the formula, R29-R32 respectively represent groups independently selected from a group comprised of hydrogen and alkyl groups having 1-4 carbons) can be mentioned.

[0041] As the ring-shaped saturated amines, piperidine, pyrrolidine, morpholine, piperazine, derivatives having these skeletons, and these ammonium hydroxide compounds are preferably used.

[0042] As the ring-shaped unsaturated amines, pyridine, α -picoline, β -picoline, γ -picoline, quinoline, isoquinoline, pyrroline, derivatives having these skeletons, and these ammonium hydroxide compounds are mentioned.

[0043] Among these basic compounds, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, ethylmethylamine, ethyldimethylamine, diethylmethylamine, pyridine, α -picoline, β -picoline, γ -picoline, etc., are especially preferably mentioned. In case these compounds are used, a polymer with especially high electric conductivity and high purity can be obtained. Also, these basic compounds (ii) can be used by mixing at an optional ratio of two kinds or more.

[0044] The concentration of these basic compounds (ii) is used in a range of 0.1 mol/L or more, preferably 0.1-10.0 mol/L, and especially preferably 0.2-8.0 mol/L. At that time, if the concentration is less than 0.1 mol/L, the yield of the polymer being obtained is lowered, and if the concentration is more than 10.0 mol/L, the electric conductivity is sometimes lowered.

[0045] The weight ratio of the compound (i) and the basic compound (ii) of the above-mentioned acidic group-substituted aniline is used in a range of (i):(ii) = 1:100-100:1, preferably 10:90-90:10. Here, if the ratio of the basic compound is low, the reactivity is lowered, and the electric conductivity is also lowered. On the contrary, if the ratio is high, the ratio for forming a salt by the acidic group and the basic compound of the polymer being obtained is increased, so that the electric conductivity is sometimes lowered.

[0046] The polymerization or copolymerization is carried out in the coexistence of these basic compounds by an oxidation polymerization using an oxidizer.

[0047] As the solvent (iii), water or a mixed solvent of water and a water-soluble organic solvent is used. In case the mixed solvent is used, the mixture ratio is optional, and water:water-soluble organic solvent = 1:100-100:1 is preferably used. Also, the water-soluble organic solvent is not particularly limited as long as it is mixed with water, however methanol, ethanol, isopropyl, acetone, acetonitrile, dimethylformamide, dimethylacetamide, etc., are preferably used.

[0048] Also, the oxidizer being used in the present invention is not particularly limited as long as the

standard electrode potential is 0.6 V or higher, however peroxodisulfuric acids such as peroxodisulfuric acid, ammonium peroxodisulfate, sodium peroxodisulfate, and potassium peroxodisulfate, hydrogen peroxide, etc., are preferably used. These oxidizers may be used in combination of two kinds or more. The amount of oxidizer being used is used in a range of 1-5 mole, preferably 1-3 mole to 1 mole monomer. At that time, it is also effective to add a transition metal compound such as iron and copper as a catalyst.

[0049] In the polymerization method of the present invention, it is important to carry out the polymerization in a system in which the oxidizer exists at a mole ratio of an equal mole or more to the monomer (i). Specifically, a reaction method that drops a monomer solution into an oxidizer solution, a method that simultaneously drops an oxidizer solution and a monomer solution at a mole ratio of an equal or more, or an appropriately combined method of them are mentioned.

[0050] pH in the system during the polymerization in the present invention is preferably 7 or less. More preferably, pH is 6 or less. Here, if pH in the polymerization reaction system exceeds 7, a side reaction is easily advanced, so that impurities and an oligomer

component are generated, thereby sometimes lowering the electric conductivity, the film formability, and the purity.

[0051] In order to maintain pH in the polymerization system at 7 or less, a proton acid can be added into the polymerization system. As the proton acid, mineral acids such as hydrochloric acid, nitric acid, sulfuric acid, and borofluoric acid, mineral acids such as hydrochloric acid, nitric acid, sulfuric acid, and borofluoric acid, super acids such as trifluoromethanesulfonic acid, organic sulfonic acids such as methanesulfonic acid, dodecylbenzenesulfonic acid, toluenesulfonic acid, and camphorsulfonic acid, high-molecular acids such as polyvinylsulfonic acid, poly-2-metnylpropane-2-acrylamidesulfonic acid, etc., are mentioned, and hydrochloric acid, nitric acid, sulfuric acid, p-toluenesulfonic acid, etc., are preferably used.

[0052] The amount of proton acid being added is not particularly limited as long as it is in the range where no oxidizer is precipitated. A mole ratio of proton acid:oxidizer = 0.01:100-50:100 is preferable, and a mole ratio of 0.01:100-45:100 is especially preferable. Here, if the amount of proton acid being added is large, the monomer is precipitated when the monomer solution is

dropped, and the reaction progress is hindered, so that impurities and an oligomer component are generated, thereby sometimes lowering the electric conductivity, the film formability, and the purity. /9

[0053] In manufacturing the highly electroconductive aniline group polymer of the present invention, stirring in the polymerization system is preferably carried out at a stirring power of 0.01-5 kw/m³.

[0054] The reaction temperature is adopted in a range of preferably 50°C or lower, especially preferably -15 to 50°C, and most preferably -10 to 40°C. Here, at a temperature higher than 50°C, a side reaction is advanced, and the electric conductivity is lowered by the change of the oxidation and reduction structure of the main chain. Also, at lower than -15°C, the reaction time is lengthened.

[0055] The sulfonic acid group or carboxyl group in the polymer being manufactured by the present invention is a group independently selected from a group comprised of free acid, alkali metal salt, alkaline-earth metal salt, ammonium salt, and substituted ammonium salt. Therefore, a polymer in a state in which these groups are not alone but are mixed can also be obtained.

[0056] Specifically, in case the polymerization is carried out in the presence of sodium hydroxide, most of the

sulfonic acid group or carboxyl group in the isolated polymer is a sodium salt. Similarly, in case the polymerization is carried out in the presence of ammonia, most of the sulfonic acid group or carboxylic acid is an ammonium salt, and in case the polymerization is carried out in the presence of trimethylamine, most of the sulfonic acid group or carboxylic acid is a trimethyl ammonium salt. Also, in case the polymerization is carried out in the presence of quinoline, most of the sulfonic acid group or carboxylic acid is obtained in a quinoline salt shape. Thus, the polymer in which part or the whole of the acidic group forms a salt can be changed to a polymer with higher purity by treating with a solution containing an acid.

[0057] The polymer is isolated by filtering from the reaction solution, however an unreacted monomer is dissolved in the reaction solution. As a separator being used at that time, pressure-reduced filtration, pressurized filtration, centrifugal separation, centrifugal filtration, etc., are employed, and especially in case a separator such as centrifugal separation and centrifugal filtration is employed, a polymer with high purity is easily obtained.

[0058] Also, as a washing solvent during the separation and purification, in case alcohols such as methyl alcohol, ethyl alcohol, iso-propyl alcohol, n-propyl alcohol, and t-

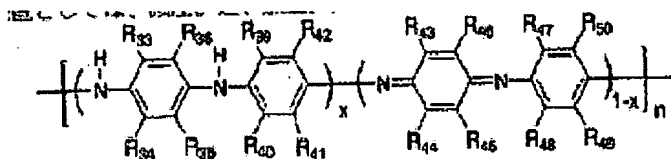
butyl alcohol, acetone, acetonitrile, N,N-dimethylformamide, N-methylpyrrolidone, and dimethyl sulfoxide are used, a polymer with high purity is obtained, and the case where methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, and acetonitrile are used is especially effective.

[0059] The weight average molecular weight of the aniline group polymer containing a sulfonic acid group or carboxyl group in an aromatic ring obtained in this manner is 5,000-3,240,000, preferably 5,000-1,000,000, and especially preferably 10,000-500,000.

[0060] This polymer can be dissolved in simple water, water containing a base such as ammonia and alkylamine or a basic salt such as ammonium acetate and ammonium oxalate, water containing an acid such as hydrochloric acid and sulfuric acid, or a solvent such as methyl alcohol, ethyl alcohol, and isopropyl alcohol, and these mixtures.

[0061] Also, it is said that the polymer or copolymer synthesized by the above method has a phenylenediamine structure (reduction type) and a quinodiimine structure (oxidation type) represented by a general formula (9).

(Structure 11)



(In the formula, R_{33} - R_{49} are selected from electron-attracting group, acidic group, hydrogen, straight-chain or branched alkyl group having 1-24 carbons, straight-chain or branched alkoxy group having 1-24 carbons, hydroxyl group, nitro group, and halogen, and at least one of them represents an acidic group. Also, the acidic group represents a sulfonic acid group or carboxyl group. Among them, especially preferably, at least two of four substituents of each aromatic ring respectively have an acidic group or alkoxy group.) The phenylenediamine structure (reduction type) and the quinodiimine structure (oxidation type) can be reversibly converted at an option ratio by the oxidation or reduction. The ratio x of the phenylenediamine structure and the quinodiimine structure is in a range of preferably $0.2 < x < 0.8$, more preferably

$0.3 < x < 0.7$ in terms of electric conductivity and solubility.

[0062] Also, the aniline group polymer of the present invention may include at least one kind of structural unit of substituted or unsubstituted aniline, thiophene, pyrrole, phenylene, vinylene, divalent other unsaturated groups, and divalent saturated group as a structural unit other than that represented by the general formula (2) unless it has an influence on the solubility, the electric conductivity, and the properties. In this case, the content of the repeated unit of the general formula (2), that is, the content of the substituted repeated unit of the acidic group to the aromatic ring is preferably 70% or more, more preferably 80% or more, and most preferably 90% or more. If the content of the substituted repeated unit of the acidic group to the aromatic ring is less than 70%, the solubility in water is sometimes insufficient.

[0063]

(Application examples)

Next, the present invention is explained by application examples. Also, the IR spectrum was measured using a device made by Perkin Elma Co. (model 1600). In the measurement of the molecular weight distribution and the molecular weight, a GPC measurement (as /10

calculated by polystyrenesulfonic acid) was carried out using an aqueous GPC column. As the column, two kinds of aqueous columns were employed by connecting. Also, as an eluent, 0.01 mol/L phosphoric acid buffer solution was used. In the measurement of pH, a glass electrode was employed. In the measurement of the electric conductivity, a four-terminal method was employed, and in the measurement of the surface resistance, a two-terminal method was employed. In the measurement of the stirring power, the power consumption of a stirrer was adopted. Also, the stirring power shows a power actually required for a polymerization solution from which seal loss, etc., are subtracted.

[0064] Application Example 1

100 mmol 2-aminoanisoole-4-sulfonic acid was dissolved at 0°C in 30 mL solution of water:acetonitrile of 3:7 of triethylamine with a concentration of 4 mol/L and dropped into 100 mL solution of water:acetonitrile of 3:7 containing 100 mmol ammonium peroxodisulfate while cooling. At that time, the monomer solution drop rate was 100 mmol/h, the stirring power was 0.7 kw/m³, the highest arrival temperature during the reaction was 15°C at a monomer drop of 0.5 equivalent. Also, pH in the reaction system was pH 3 at a time of the reaction start and pH 1.5

at a time of the drop end. When the lowest value of pH was 1.0, the monomer drop equivalent was 0.6 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a centrifugal filter, washed with methyl alcohol, and dried, so that 17 g polymer powder was obtained. Its volume resistance value was 0.2 S/cm. Also, the 2-aminoanisole-4-sulfonic acid as a residual monomer being included in this polymer was 0.2%, and the triethylamine sulfate as a by-produced salt was 0.05%.

[0065] The above-mentioned polymer at 5 parts by weight was stirred and dissolved at room temperature in water at 100 parts by weight, so that an electroconductive composition was prepared. The solution obtained in this manner was spread on a glass substrate by a spin-coating method and dried at 100°C. A film with a surface resistance value of $3 \times 10^4 \Omega/\square$ having a smooth surface with a film thickness of 0.2 μm was obtained. As a result of its measurement, the number average molecular weight MN was 25,000, the weight average molecular weight MW was 27,000, the Z average molecular weight was 28,000, and the degree of dispersion $MW/MN = 1.08$ and $MZ/MW = 1.04$.

[0066] When the polymer was added little by little to 10 mL water, 0.1 mol/L aqueous sulfuric acid solution, or 0.1

mol/L ammonia water and was not dissolved, it was filtered, and the amount dissolved was attained. As a result, the solubility of the electroconductive polymer synthesized in Application Example 1 was 370 mg/mL in water, 310 mg/mL in 0.1 mol/L aqueous sulfuric acid solution, and 420 mg/mL in 0.1 mol/L ammonia water.

[0067] Application Example 2

100 mmol 2-methyl-4-aminobenzenesulfonic acid was dissolved at 10°C in 25 mL solution of water:acetonitrile of 5:5 of trimethylamine with a concentration of 4 mol/L and dropped into 100 mL solution of water:acetonitrile of 5:5 containing 100 mmol ammonium peroxodisulfate while cooling. At that time, the monomer solution drop rate was 50 mmol/h, the stirring power was 1.0 kw/m³, the highest arrival temperature during the reaction was 20°C at a monomer drop of 0.4 equivalent. Also, pH in the reaction system was pH 3 at a time of the reaction start and pH 2 at a time of the drop end. When the lowest value of pH was 1.0, the monomer drop equivalent was 0.4 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a centrifugal filter, washed with methyl alcohol, and dried, so that 13 g polymer powder was obtained. Its volume resistance value was 0.18 S/cm. Also, the 2-methyl-4-aminobenzenesulfonic acid as a

residual monomer being included in this polymer was 0.5%, and the trimethylamine sulfate as a by-produced salt was 0.1%.

[0068] Application Example 3

1 mol 2-aminoanisole-4-sulfonic acid was dissolved at -3°C in 500 mL solution of water:acetone of 3:7 of triethylamine with a concentration of 2 mol/L and dropped into 1,000 mL solution of water:acetone of 3:7 containing 100 mol ammonium peroxodisulfate and 1 mol ammonium peroxondisulfate while cooling. At that time, the monomer solution drop rate was 1 mol/h, the stirring power was 1.5 kw/m³, the highest arrival temperature during the reaction was 20°C at a monomer drop of 0.7 equivalent. Also, pH in the reaction system was pH 1 at a time of the reaction start and pH 1 at a time of the drop end. When the lowest value of pH was 0.8, the monomer drop equivalent was 0.7 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a centrifugal filter, washed with methyl alcohol, and dried, so that 750 g polymer powder was obtained. Its volume resistance value was 0.25 S/cm. Also, the 2-aminoanisole-4-sulfonic acid as a residual monomer being included in this polymer was 0.15%, and the triethylamine sulfate as a by-produced salt was 0.1%.

[0069] Application Example 4

5 mol ammonium hydroxyaminobenzenesulfonate was dissolved at -3°C in 1,250 mL solution of water:isopropane of 3:7 of triethylamine with a concentration of 4 mol/L and dropped into 4,000 mL solution of water:isopropanol of 3:7 containing 5 mol ammonium peroxodisulfate and 1 g hydrochloric acid while cooling. At that time, the monomer solution drop rate was 2 mol/h, the stirring power was 0.1 kw/m³, the highest arrival temperature during the reaction was 10°C at a monomer drop of 0.2 equivalent. Also, pH in the reaction system was pH 1 at a time of the reaction start and pH 1.4 at a time of the drop end. When the lowest value of pH was 0.9, the monomer drop equivalent was 0.7 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a centrifugal filter, washed with methyl /11 alcohol, and dried, so that 14 g polymer powder was obtained. Its volume resistance value was 0.15 S/cm. Also, the hydroxyaminobenzenesulfonic acid as a residual monomer being included in this polymer was 0.2%, and the triethylamine sulfate as a by-produced salt was 0.1%.

[0070] Application Example 5

100 mmol 2-carboxylaniline (anthranilic acid) was dissolved at 5°C in 50 mL solution of water:methyl alcohol

of 3:7 of pyridine with a concentration of 2 mol/L and dropped into 100 mL solution of water:methyl alcohol of 3:7 containing 100 mmol ammonium peroxodisulfate while cooling. At that time, the monomer solution drop rate was 50 mmol/h, the stirring power was 0.8 kw/m³, the highest arrival temperature during the reaction was 13°C at a monomer drop of 0.5 equivalent. Also, pH in the reaction system was pH 3 at a time of the reaction start and pH 3 at a time of the drop end. When the lowest value of pH was 1.5, the monomer drop equivalent was 0.5 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a centrifugal filter, washed with methyl alcohol, and dried, so that 8 g polymer powder was obtained. Its volume resistance value was 0.1 S/cm. Also, the anthranilic acid as a residual monomer being included in this polymer was 0.2%, and the pyridine sulfate as a by-produced salt was 0.1%.

[0071] Comparative Example 1

100 mmol 2-aminoanisoole-4-sulfonic acid was dissolved at 25°C in 30 mL aqueous ammonia solution with a concentration of 4 mol/L and dropped into 100 mL aqueous solution containing 100 mmol ammonium peroxodisulfate while cooling. At that time, the oxidizer drop rate was 100 mmol/h, the stirring power was 0.1 kw/m³, the highest

arrival temperature during the reaction was 55°C at an oxidizer drop of 0.2 equivalent. Also, pH in the reaction system was pH 11 at a time of the reaction start and pH 3 at a time of the drop end. When the lowest value of pH was 1.5, the oxidizer drop equivalent was 0.2 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a filter, washed, and dried, so that 8 g polymer powder was obtained. Its volume resistance value was $< 0.0001 \text{ S/cm}$. Also, the 2-aminoanisole-4-sulfonic acid as a residual monomer being included in this polymer was 6%, and the ammonium sulfate as a by-produced salt was 8%.

[0072] The above-mentioned polymer at 5 parts by weight was stirred and dissolved at room temperature in water at 100 parts by weight, so that an electroconductive composition was prepared. The solution obtained in this manner was spread on a glass substrate by a spin-coating method and dried at 100°C, however a uniform film could not be obtained. The electric conductivity of the film obtained was $1 \times 10^9 \text{ } \Omega/\square$. As a result of the measurement of the molecular weight, the number average molecular weight M_N was 1,400, the weight average molecular weight M_W was 8,000, the Z average molecular weight was 3,300, and the degree of dispersion $M_W/M_N = 5.7$.

[0073] Comparative Example 2

100 mmol 2-carboxylaniline (anthranilic acid) was dissolved at 25°C in 50 mL aqueous pyridine solution with a concentration of 6 mol/L and dropped into 100 mL solution containing 100 mmol ammonium peroxodisulfate while cooling. At that time, the oxidizer solution drop rate was 50 mmol/h, the stirring power was 0.3 kw/m³, the highest arrival temperature during the reaction was 35°C at an oxidizer drop of 0.3 equivalent. Also, pH in the reaction system was pH 12 at a time of the reaction start and pH 7 at a time of the drop end. When the lowest value of pH was 7, the oxidizer drop equivalent was 0.3 equivalent. After finishing the drop, stirring was further carried at 25°C for 12 h, the reaction product was filtered by a filter, washed, and dried, so that 3 g polymer powder was obtained. Its volume resistance value was 0.001 S/cm. Also, the anthranilic acid as a residual monomer being included in this polymer was 9%, and the pyridine sulfate as a by-produced salt was 7%.

[0074] Comparative Example 3

As an aniline group electroconductive polymer, sulfonated polyaniline was synthesized according to the known method (J. Am. Chem. Soc., (1991), 113, 2665-2666). The above-mentioned sulfonated polyaniline at 3 parts by

weight was stirred and dissolved at room temperature in 0.2 mol/L aqueous sulfuric acid solution at 100 parts by weight, so that an electroconductive composition was prepared. The solution obtained in this manner was spread on a glass substrate by a spin-coating method, however since it was insoluble in 0.2 mol/L aqueous sulfuric acid solution, no film was formed.

(Effects of the invention)

According to the present invention, an aniline group polymer that exerts high electric conductivity, has high purity, has a molecular weight distribution close to a monodisperse, and exhibits excellent solubility in water or organic solvents at any pH can be obtained. Also, in this reaction, since a side reaction is difficult to be generated, impurities and an oligomer component are difficult to be generated. As a result, a highly electroconductive high-purity aniline group polymer in which the average molecular weight is improved, the electric conductivity is largely improved, and the hue and the film formability are also improved can be obtained by a simple manufacturing method.